A STUDY OF INHALATION EXPOSURES OF TARPAULIN FUMIGATION WORKERS TO METHYL BROMIDE IN MERCED COUNTY, CALIFORNIA IN NOVEMBER 1982

by

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SUMMARY

In November 1982, inhalation exposure monitoring was conducted on a worker performing methyl bromide tarpaulin fumigations on raisins. The fumigations were done in the field, at least 100 feet from the nearest structure. The temperatures during the monitoring were in the 50°F range. The worker was monitored during two applications of the fumigant and once during removal of the tarpaulin covering the commodities. The highest level found was 1.8 parts per million (ppm) measured over a nine minute period during one application. This is well below the permissable exposure level of 15 ppm. Area measurements taken around the fumigation site were below 1 ppm.

INTRODUCTION

Methyl bromide (bromomethane, CH_3Br) is a broad spectrum pesticide which has a variety of uses as a fumigant including commodity treatment. It is normally sold as a pressurized liquid. Methyl bromide is extremely hazardous with a inhalation LC_{50} of 200 ppm in rats. The Cal/OSHA permissable exposure level (PEL) for methyl bromide is 15 ppm over a 8 hour workday, 40 hour work week. The short term excursion level (STEL) is 25 ppm for 5 minutes. The ceiling level is 50 ppm which cannot be exceeded at any time.

MATERIALS AND METHODS

Air concentrations were measured by drawing air through charcoal sampling tubes with an MSA Model C-210 air sampling pump. The pumps were operated at a maximum flow of approximately 0.2 liters/minute. The sampling tubes were placed in the worker's breathing zone. Tygon tubing connected the charcoal sampling tube to the air pump on the worker's belt. The MSA C-210 air pump is a piston cylinder-displacement pump of known displacement. The number of piston strokes were counted during the monitoring interval and multiplied by the cubic displacement of the cylinder. This yielded the total air volume which was then corrected for barometric pressure and temperature. After each monitoring interval the air tubes were capped, frozen and delivered to the CDFA Lab in Sacramento within 48 hours. The method for determination of methyl bromide on charcoal tubes is in Appendix I.

Eight raisin bins were fumigated on November 3rd. The bins were placed side by side in two rows of four and draped with a polyethylene tarp. The tarp was sealed to the ground with dirt. A piece of wood embedded with a nail was placed under the tarp and positioned against a one and a half pound can of methyl bromide. The applicator punctured the can by stepping on the tarp over the nail. He then inspected for gaps between the tarp and the ground. He had no method available on site to test for leaks. The applicator conducted a similar fumigation on November 8th. Two sets of tarped bins were fumigated, each set had two rows of six bins, and two one and a half pound cans of methyl bromide were used under each tarp.

Two air samples were taken 25 feet downwind during both applications, each for 30 minutes, beginning with the first methyl bromide can puncture. An air sample was also taken between the 2 sets of tarped bins fumigated on November 8th.

Removal of the fumigation tarps was monitored on November 11. The tarps were pulled away from the bins, breaking their seal with the ground, and then pulled off the tops of the bins. This task required 17 minutes.

Three area samples were taken during the tarp removal, each lasting for 30 minutes, beginning when the worker first began to pull up the tarps. Two of the area samples were taken 25 feet downwind, and the third was taken between the two stacks of bins. The fumigation site was located in the field, at least 100 feet from the nearest structure. The temperature was in the 50°F range during the monitoring.

RESULTS

Location	Date	Time Sample	Concentration
Applicator (personal sample)	11/03	13 minutes	0.09 ppm
Applicator (personal sample)	11/08	9 minutes	1.79 ppm
Tarp removal (personal sample)	11/11	17 minutes	0.86 ppm
25 feet downwind (application)	11/03	30 minutes	Less than 0.006 ppm
25 feet downwind (application)	11/03	30 minutes	Less than 0.006 ppm
25 feet downwind (application)	11/08	30 minutes	0.08 ppm
25 feet downwind (application)	11/08	30 minutes	0.31 ppm
between tarped bins (application)	11/08	30 minutes	0.02 ppm
between tarped bins (tarp removal)	11/11	31 minutes	0.59 ppm
25 feet downwind (tarp removal)	11/11	31 minutes	0.03 ppm

CONCLUSION

This worker annually uses methyl bromide over a six week period for a total of about 20 hours of possible exposure. In this case, when he follows the work practices described, methyl bromide exposure should be well below levels considered to be hazardous.

APPENDIX I

DETERMINATION OF
METHYL BROMIDE ON CHARCOAL TUBES

Scope

This method is for the desorption and analysis of methyl bromide from charcoal air sampling tubes. It is intended solely for the use of the California Department of Food and Agriculture, Chemistry Laboratory Services.

Principle

Methyl bromide (MeBr) that has been adsorbed from the air onto activated charcoal is desorbed from the charcoal with ethyl acetate, diluted as needed and analytically determined by gas chromatography using flame ionization or electron capture detection.

Reagents and Equipment

1. Ethyl acetate, nanograde.
2. Analytical grade methyl bromide.
3. Approved and calibrated personal sampling pump.
4. Charcoal tubes--SKC #226-09.
5. Developing vials with teflon liners--SKC #226-02.
6. Assorted microsyringes for preparing standards and gas chromatography.
7. Assorted pipets.
8. Volumetric flasks.
9. Small triangular file for scoring glass tubes.
10. Gas sampling bulb--Supelco 500 ml. with septum (#2-2148).

Analysis

Interferences: High humidity may affect trapping efficiency.

1. Score each charcoal tube with a file in front of the first section of charcoal.
2. Break open the tube. Remove and discard the glass wool.
3. Transfer the charcoal in the upstream section to a labeled desorption vial which contains a known amount of nanograde ethyl acetate. 2-4 ml. is suggested. Adding solvent to the charcoal may cause loss of MeBr.

4. Remove and discard the foam partition from the tube.

5. Transfer the second section of charcoal to a second labeled desorption vial which contains a known amount of nanograde ethyl acetate.

6. Allow the samples to desorb for one hour while rotating @30 rpm.

7. Transfer an aliquot to a sample storage vial, label, and freeze until analysis time.

8. Determine by GLC.

Determination of Desorption Efficiency

1. Inject a known amount of MeBr (1 microgram to several milligrams) into the charcoal with a syringe and cap the tube with the supplied caps. The tube should be from the same lot that was used for the samples.

2. At least five tubes (preferably at levels covering the expected range) should be prepared in this manner and allowed to stand at least overnight to assure complete adsorption. A blank tube should be treated the same way except that no sample is added.

3. Analyze the tubes by the analytical procedure.

4. Desorption efficiency = $\frac{\text{Response sample-response blank}}{\text{Response standard}}$

   The standard(s) should be the same amount as injected into the charcoal tubes. This eliminates standard variation errors.

Calculations

1. Determine weight of MeBr present on charcoal tube sections by GLC analysis.

2. Correct this total weight of MeBr by subtracting any blank value present on the blank tube.

3. The corrected weight is divided by the desorption efficiency to obtain the final weight of MeBr present.

4. The volume of air sampled is converted to standard conditions of 25°C and 760 mm Hg.

$$VS = \frac{V \times P \times 298}{760 \times (T+273)}$$

Where VS = Volume of air at standard conditions.
V = Volume of air as measured.
P = Barometric pressure in mm Hg.
T - Temperature of air in °C.

5. Calculate ppb in air from the above data.

$$\text{ppb (volume basis)} = \frac{\text{ng} \times 24.45}{\text{VS} \times 94.9} \quad \frac{\text{ng}}{\text{VS}} \times 0.2576$$

24.45 is the mole volume of MeBr at 25° and 760 mm.
94.9 is the molecular weight of MeBr.

Gas Chromatographic Conditions

Gas chromatograph with Ni^{63}, H^3, or flame ionization detector.

Temperatures - Injector: 125°C
Detector: Follow manufacturer's suggestions

Column: 20' x 1/8" O.D. nickel tubing
10% SP-2100 on 100/120 Chromosorb W-HP
70°C, 10 ml/min N_2 carrier gas
MeBr retention time approximately 1.9 minutes

Column: 6' x 2 mm I.D. glass
80/100 Poropak Q
130°C, 30 ml/min N_2 carrier gas
MeBr retention time approximately 1.4 minutes

Column: 20' x 1/8" O.D. nickel tubing
10% FFAP on 100/120 Chromosorb W-HP
70°C, 25 ml/min N_2 carrier gas
MeBr retention time approximately 1.9 minutes

References

1. NIOSH Manual of Analytical Methods, Second Edition. Method S372. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., 20402.

2. Determination of EDB on Charcoal Tubes, California Department of Food and Agriculture, Chemistry Laboratory Services, 3292 Meadowview Road, Sacramento, California 94832.

3. Mr. Mario Fraccia, Air Industrial Hygiene Lab, Berkeley, California. Personal Communication.